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character from  $H$  and  $OH$ , no such simple behavior is to be expected, nor is it found. Rules for such systems have still to be discovered.

The reason for the above dependence of solubility upon compound formation becomes evident when we examine the freezing-point depression curve of a system such as  $Li_2SO_4-H_2SO_4$ . The absolute freezing-point of the salt is so high that, unless compound formation took place, solubility in the acid at ordinary temperatures would, according to the Schröder-Le Chatelier equation,<sup>4</sup> necessarily be negligible. The removal of simple solute molecules by combination with solvent, however, results in an increased solubility, and the extent of such increase depends, naturally, upon the extent of compound formation. The further development of this topic and the presentation of quantitative results will be given in forthcoming articles in the *Journal of the American Chemical Society*.

\* Contribution No. 350.

<sup>1</sup> Kendall and Booge, *J. Amer. Chem. Soc.*, **39**, 1917 (2323).

<sup>2</sup> Carpenter, Ph.D. *Dissertation*, Chicago, 1915; Gibbons, *J. Amer. Chem. Soc.*, **37**, 1915 (149); Booge, Ph.D. *Dissertation*, Columbia, 1916; Gross, Ph.D. *Dissertation*, Columbia, 1919; Landon, Ph.D. *Dissertation*, Columbia, 1920; Adler, Ph.D. *Dissertation*, Columbia, 1920; Davidson, Ph.D. *Dissertation*, Columbia, 1920.

<sup>3</sup> Kendall and Booge, *loc. cit.*; Gross, *loc. cit.*

<sup>4</sup> Roozeboom, *Heterogene Gleichgewichte*, **2**, 1904 (270-84).

## THE PELTER EFFECT

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When a current of electricity goes from metal  $\alpha$ , in which the free-electron fraction of the conductivity is  $(k_f \div k)_\alpha$ , to the metal  $\beta$ , in which the corresponding fraction is  $(k_f \div k)_\beta$ , ionization or reassociation must take place at the junction, according as  $(k_f \div k)_\beta$  is greater or less than  $(k_f \div k)_\alpha$ . The resulting change of condition is the same whether we assume the ionization or reassociation to take place after or before the crossing of the interface between  $\alpha$  and  $\beta$ . We shall use each of these hypotheses in turn, beginning with the first.

The gain of energy, and so the heat energy absorbed, by the unit quantity of electricity, 10 coulombs, in the form of electrons, in crossing the boundary from  $\alpha$  to  $\beta$  is

$$\Pi = \left(\frac{k_f}{k}\right)_\alpha (P_\beta - P_\alpha)_f + \left(\frac{k_a}{k}\right)_\alpha (P_\beta - P_\alpha)_a + (P_\beta - P_\alpha) + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right] \lambda_\beta, \quad (1)$$

where  $(P_\beta - P_\alpha)_f$  means the  $P_f$  of  $\beta$  minus the  $P$  of  $\alpha$ , etc., the nomenclature according in general with that of my preceding papers.

From my paper in these PROCEEDINGS for April, 1918, we get, by integration of equation (5) there given,

$$(P_\beta - P_\alpha) = -(P_\beta - P_\alpha)_\alpha. \quad (2)$$

Integrating equation (6) of the same paper, we get

$$(P_\beta - P_\alpha) + (P_\beta - P_\alpha)_f = - \int_\alpha^\beta \frac{dp}{ne} = - \frac{RT}{e} \int_\alpha^\beta \frac{dn}{n} = \frac{RT}{e} \cdot \log_e \frac{n_\alpha}{n_\beta}. \quad (3)$$

From (1), (2) and (3) we get

$$\Pi = \left(\frac{k_f}{k}\right)_\alpha \frac{RT}{e} \cdot \log_e \frac{n_\alpha}{n_\beta} + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right] \lambda_\beta. \quad (4)$$

If we had used at the beginning the hypothesis that the ionization occurred in  $\alpha$ , just before the crossing, we should have obtained the expression

$$\Pi = \left(\frac{k_f}{k}\right)_\beta \frac{RT}{e} \cdot \log_e \frac{n_\alpha}{n_\beta} + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right] \lambda_\alpha. \quad (5)$$

The total change of state being the same in the process which gives equation (5) as in that which gives equation (4), the total heat absorbed must be the same in both cases—that is, the  $\Pi$  of (5) is the same as the  $\Pi$  of (4).

Subtracting (5) from (4) we get

$$\left[\left(\frac{k_f}{k}\right)_\alpha - \left(\frac{k_f}{k}\right)_\beta\right] \frac{RT}{e} \cdot \log_e \frac{n_\alpha}{n_\beta} + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right] (\lambda_\beta - \lambda_\alpha) = 0, \quad (6)$$

whence

$$\lambda_\beta - \lambda_\alpha = \frac{RT}{e} \cdot \log_e \frac{n_\alpha}{n_\beta}, \quad (7)$$

or

$$\frac{n_\alpha}{n_\beta} = e^{\frac{(\lambda_\beta - \lambda_\alpha)e}{RT}}. \quad (8)$$

Equation (8) has a familiar form, and in fact it might have been written down at once without circumlocation as soon as the fact was recognized, as it was in my paper of April, 1918, that the free electrons in the one metal are in equilibrium with those in the other, there being no circulatory motion of the electrons at the junction if the metals are at one temperature.

Making use of equation (7) we can change (4) to the form

$$\Pi = \left(\frac{k_f}{k}\right)_\alpha (\lambda_\beta - \lambda_\alpha) + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right] \lambda_\beta, \quad (9)$$

and so

$$\Pi = \left(\frac{k_f}{k}\right)_\beta \lambda_\beta - \left(\frac{k_f}{k}\right)_\alpha \lambda_\alpha. \quad (10)$$

It is now in order to see how well values of  $\Pi$  calculated by means of

this formula, with the tentative values of  $(k_f \div k)$  and  $\lambda$  obtained for each metal in my paper on the Thomson Effect and Thermal Conduction,<sup>1</sup> agree with those found by Bridgman from his experiments. Close agreement is, of course, not to be expected, even if my theory is everywhere correct, for the values of  $(k_f \div k)$  and  $\lambda$  given in the paper just mentioned were obtained without any regard whatever for the Peltier effect, they being merely certain values, not the only values, that will, approximately at least, meet the requirements of the Thomson effect and thermal conductivity. Moreover, the experimental data used in arriving at these values are doubtless faulty in many particulars; for example, in a number of cases I had no observed value of the thermal conductivity at 100° C., and was obliged to make use of a value calculated, not very safely, by means of the Wiedemann-Franz law.

Departing from the common practice, I have substituted bismuth for lead as the reference metal, taking as my definition of the Peltier heat the amount of heat (ergs) absorbed in the passage of  $(1 \div e)$  electrons from any given metal to bismuth. All the values in the table below are to be multiplied by  $10^4$ . *Con.* is constantan and *Man.* is manzanin.

TABLE I  
THE PELTIER HEAT

	OF VARIOUS METALS AGAINST BISMUTH								
	At 0° C.				At 100° C.				
	I Obs.	II Calc. 1	III Calc. 2	IV Calc. 3	V Obs.	VI Calc. 1	VII Calc. 2	VIII Calc. 3	IX V-VIII
Fe	247	798	311	251	310	861	323	226	84
Mo	219	814	327	217	319	911	373	252	67
Zn	211	822	335	212	274	904	366	225	49
Au	211	804	317	210	280	888	350	227	53
Cu	211	817	330	211	280	905	367	229	51
Ag	210	831	344	209	279	925	387	226	53
Tl	208	778	291	209	271	850	312	221	50
W	207	748	261	208	285	822	284	234	51
Sn	204	799	312	204	266	880	342	220	46
Mg	203	769	282	202	266	846	308	220	46
Al	202	772	285	201	263	844	306	210	53
Pt	195	783	296	194	245	847	309	195	50
Pd	188	747	260	188	232	795	257	182	50
Co	156	645	158	154	172	642	104	117	55
Ni	155	650	163	153	187	668	130	136	51
Bi	0	0	0	0	0	0	0	0	0
Con.	108	533	36	108	106	493	—45	55	51
Man.	207	591	104	206	275	604	66	223	52

Column I gives the observed, or experimentally found, values of II, with respect to bismuth, at 0° C. Column II gives the values calculated,

by means of equation (10), from the values of  $(k_f \div k)$  and  $\lambda$ , for  $0^\circ \text{ C.}$ , given in my already printed paper on the Thomson Effect and Thermal Conduction. Comparison of these two columns shows that the calculated values are three or four times as great as the observed values, but this disparity, before any adjustments have been attempted, is not discouraging.

Column V gives the observed values for  $100^\circ \text{ C.}$ , while VI gives those found by means of equation (10) from the values of  $(k_f \div k)$  and  $\lambda$ , for  $100^\circ \text{ C.}$ , given in the paper just mentioned. Here again the calculated values are some-fold larger than the observed values.

Columns III and VII, which are to be compared with I and V, respectively, are obtained from columns II and VI, respectively, merely by using new values of  $(k_f \div k)$  and  $\lambda$ , for bismuth, these new values serving quite as well as the former ones, on the whole, for the Thomson effect and the thermal conductivity of bismuth.

Columns IV and VIII, which are to be compared with I and V, respectively, are obtained from III and VII, respectively, by using new values of  $(k_f \div k)$  and  $\lambda$  for each of the other metals than bismuth, due regard being paid to the Thomson effect and the thermal conductivity in the selection of these new values.

The agreement between columns I and IV is as good as need be. The agreement between columns V and VIII is not so good, the values in V being in every case the larger, as column IX shows. A new readjustment in the case of bismuth, making  $[(k_f \div k)\lambda]_{100}$  for this metal about 14% greater than the last re-adjustment left it, would reduce most of the differences shown in column IX to a negligible size. But such a re-adjustment cannot be made without introducing disagreements at other points. The disparities between columns V and VIII, together with equally serious disparities, at  $100^\circ \text{ C.}$ , between thermal conductivities given by my formulae and those found by other means, must stand for the present.

A plausible explanation of these discrepancies, where they are not to be accounted for by mere imperfection of experimental data, may be found in the crudity of my assumption that the number,  $n$ , of free electrons per cu. cm. of a metal, can be expressed by the formula

$$n = zT^q$$

where  $z$  and  $q$  are constants. In making this assumption I did not expect it to hold for so great a range of temperature as that between  $0^\circ$  and  $100^\circ \text{ C.}$  In fact, I was greatly surprised to find, a year or so ago, that I could make the jump from  $0^\circ$  to  $100^\circ$  with any measure of success.

It is interesting to inquire how the theory of the Peltier effect set forth in this paper can deal with Bridgman's observations on the magnitude and sign of this effect between compressed and uncompressed pieces of the same metal. Testing twenty metals, including two alloys, he measured the heat absorbed by unit quantity of "positive electricity in passing from uncompressed metal to [the same] metal compressed" or, as I prefer to

put it, by  $(1 \div e)$  electrons in passing from the compressed to the uncompressed metal. Working from 1 atm. to 2000 kgm./cm.<sup>2</sup> and from 0° C. to 100° C., he found this absorption to be positive throughout in fourteen of the metals; negative throughout in three, cobalt, magnesium, and manganin; mixed, sometimes positive and sometimes negative, in three, aluminium, iron, and tin.

In terms of my theory a positive effect here can be accounted for by a decrease of  $(k_f \div k)\lambda$  under pressure, and a negative effect by an increase. It seems probable that  $(k_f \div k)$  is generally decreased by pressure, and that the increase of  $(k_f \div k)\lambda$  indicated for certain cases by Bridgman's experiments is to be attributed to an increase of  $\lambda$  sufficient to overbalance the decrease of  $(k_f \div k)$ . *A priori* one might expect  $\lambda$  to decrease with increase of pressure, causing reduction of volume, since, according to the formula  $\lambda' = \lambda_c' + sRT$ , it increases with rise of temperature, causing expansion. But it is unsafe to assume that a contraction caused by pressure will have the same effect on the properties of a substance as a contraction caused by fall of temperature. Thus Bridgman says:<sup>2</sup> "The volume of many metals at 0° C. and 12,000 kg. [per cm.<sup>2</sup>] is less than the volume at atmospheric pressure at 0° Abs. The resistance of most metals tends towards zero at 0° Abs., but at 0° C. at the same volume the resistance is only a few per cent less than under normal conditions."

A change of about 8% in the value of  $(k_f \div k)\lambda$  would account for the maximum Peltier effect between compressed and uncompressed bismuth, as observed by Bridgman, and a still smaller per cent change, in most cases much less than one per cent, would serve for the other metals dealt with in this paper.

<sup>1</sup> These PROCEEDINGS, October, 1920, p. 613.

<sup>2</sup> *Proc. Amer. Acad. Arts & Sci.*, **52**, No. 9 (638).

## ON THE ROOTS OF BESSEL'S FUNCTIONS

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The roots of the equation  $J_n(z) = 0$  are known to be all real if  $n < -1$ . The methods of Sturm when applied to the function  $J_n(z)$  show that the roots are increasing functions of  $n$  if  $n > 0$ , that is to say, denoting by  $\psi_k(n)$  the  $k^{\text{th}}$  positive root  $\psi_k(n') > \psi_k(n)$  if  $n' > n > 0$ . In the following it will be shown that  $\psi_k(n') > \psi_k(n)$  if  $n' > n > -1$  so that the inequality holds as well when  $-1 < n < 0$ .

Putting  $f_n(z) = \sum \frac{z^r}{\Gamma(n+r+1)\Gamma(r+1)}$  so that  $J_n(z) = \left(\frac{z}{2}\right)^n f_n\left(-\frac{z^2}{4}\right)$  the polynomials  $g^n(z)$  are to be considered. They satisfy the recurrence